



Comment on the paper “Effect of stress on dissolution/precipitation of platinum: Implications concerning core–shell catalysts and cathode degradation in proton exchange membrane fuel cells” by Preethy Parthasarathy, Anil V. Virkar* [J. Power Sources 196 (2011) 9204–9212]

A B S T R A C T

Keywords:

Stress
Electrode potential
Chemical potential
Platinum
Silver

Electrode potential of a metal changes by applied mechanical stress. This effect was experimentally determined both by Parthasarathy and Virkar [J. Power Sources 196 (2011) 9204–9212] and by the present authors [Phys. Chem. Chem. Phys., 3 (2001) 2662–2667]. The aim of the present Comment is to dispel a misunderstanding regarding the interpretation of the observations.

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Recently Parthasarathy and Virkar [1] investigated the dissolution/precipitation of platinum as influenced by applied stress. Part of their experimental setup consisted of a platinum wire or foil immersed in a $\text{PtCl}_4/\text{DMSO}$ solution; the metal was exposed to tensile stress by loading the sample with various standard weights and its potential was measured against a similar but unstressed metal electrode. The stressed electrode was always found more positive than the unstressed one the difference being proportional with stress. Varying somewhat with the wire diameter the proportionality coefficient was around $16\text{--}20\text{ }\mu\text{V MPa}^{-1}$ determined under open circuit conditions.

Earlier we carried out similar experiments with silver wires immersed into aqueous AgNO_3 solutions [2]. We observed similar proportional changes of the same sign with coefficients between 6 and $9\text{ }\mu\text{V MPa}^{-1}$ varying with solute concentrations. We used the same diameter wire throughout the experiments.

We find it most rewarding that systems, as different as those used in the two works cited, behave in a much similar manner. The comparison of Fig. 5 in Ref. [1] with Fig. 7 in Ref. [2] clearly reveals this similarity. Despite the differences in both the solvents and the mechanisms of the electrode reactions the observations are consonant. However, at present we are not able to make a quantitative assessment of the numerical differences, since the potential of zero charge of the Pt/PtCl_4 electrode in the non-aqueous solution is not known to us. This parameter would be needed for the comparison of the results in terms of our theoretical interpretation [2].

Given the qualitative agreement between the experimental results we find it difficult to understand the statement made by the authors of Ref. [1]: “...the application of a tensile load/stress (leading to negative pressure) to a platinum wire/foil lowers the

chemical potential of Pt compared to the unstressed wire/foil. In some of the literature, it has been often assumed that applied stress always increases the chemical potential through the strain energy term [2].” The authors maintain that this assertion, attributed to us, is erroneous.

Erroneous it must be! We did not make any similar statement either. Since the sign of the observed voltage changes are the same in both their work and ours it would be impossible to construct interpretations which would result in changes of opposite signs. Obviously, we did not do that.

It is not clear whether Parthasarathy and Virkar mean standard state or actual chemical potential. Nevertheless, chemical potential and electrode potential are of opposite sign and they obviously know this as it is witnessed by their Eqs. (4)–(10). If so, an increase in electrode potential is tantamount to a decrease in chemical potential. Since both they and we observed similar changes in the electrode potentials there cannot exist any disagreement regarding the sign of the chemical potential change.

This misunderstanding, however, shows that we failed to explain clearly what we meant. Thus it seems advisable to give a short account on the relevant part of our ideas, set forth in Ref. [2]. Having critically evaluated three models, both as far as functional forms and numerical values were concerned, we arrived at the conclusion that the model, denoted by us as “electrostatic”, deserved a detailed analysis. This model describes the observed stress-induced change in voltage, $\Delta\varphi_{\text{obs}}$, as the algebraic sum of two terms.

The first term gives the change of the double layer potential, $\Delta\varphi_{\text{dl}}$: this change is due to the fact that the *surface area of the stressed wire is larger than that of the unstressed one*, whereas the total surface charge remains unchanged due to the open circuit condition. If one knows the elastic properties of the metal and the potential of zero charge at the metal/liquid interface, φ_0 , one can evaluate $\Delta\varphi_{\text{dl}}$ as

$$\Delta\varphi_{\text{dl}} = -(\varphi - \varphi_0)(1 - \nu)\kappa\sigma,$$

where σ denotes the stress, ν the Poisson ratio, κ the isothermal compliance coefficient for tensile stress, φ the potential of the unstrained wire and φ_0 the potential of zero charge, both measured against the same reference electrode. For the sake of clarity we use here the notation of Ref. [1].

The second term accounts for the change of the potential of zero charge, $\Delta\varphi_0$: this change is due to the fact that *the volume of the stressed wire is larger than that of the unstressed one*. This formally writes, in linear approximation, as

$$\Delta\varphi_0 = \frac{\partial\varphi_0}{\partial\sigma}\sigma.$$

The observed change in potential is described as

$$\Delta\varphi_{\text{obs}} = \Delta\varphi_{\text{dl}} + \Delta\varphi_0.$$

The left hand of the above equation is measured, the first term on the right hand side can be calculated from independent data, hence the only remaining term can be evaluated. We found the value $(\partial\varphi_0/\partial\sigma)_{\text{obs}} = 25.6 \pm 1 \text{ } \mu\text{V MPa}^{-1}$. Clearly, the potential of zero charge increases, thus the corresponding chemical potential decreases under stress, as it is postulated in Ref. [1].

We went one step further and compared the above experimental value with a theoretical estimate. A simple calculation, based on the Sommerfeld model of electrons in a conductor,

resulted in $(\partial\varphi_0/\partial\sigma)_{\text{calc}} \cong 20.4 \text{ } \mu\text{V MPa}^{-1}$. The reasonable agreement between experiment and theory lends some support to the understanding proposed by us.

Thus we think that the statement of Parthasarathy and Virkar on a surmised error of ours stems from misunderstanding. One further comment, however, might be well in order. A discussion on similar results [3,4] have shown clearly that, beyond the mechanical properties of the metal, also the chemical composition of the electrolyte plays an important role in the process.

References

- [1] P. Parthasarathy, A.V. Virkar, J. Power Sources 196 (2011) 9204–9212.
- [2] Á. Horváth, R. Schiller, Phys. Chem. Chem. Phys. 3 (2001) 2662–2667.
- [3] Á. Horváth, G. Nagy, R. Schiller, Phys. Chem. Chem. Phys. 12 (2010) 7290.
- [4] M. Smetanin, Q. Deng, D. Kramer, S. Mohanan, U. Herr, J. Weissmüller, Phys. Chem. Chem. Phys. 12 (2010) 7291–7292.

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Available online 10 November 2012